

# PATENT COOPERATION TREATY

From the  
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

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NOTIFICATION OF TRANSMITTAL OF  
THE INTERNATIONAL PRELIMINARY  
REPORT ON PATENTABILITY  
(PCT Rule 71.1)

Date of mailing  
(day/month/year) 20.06.2005

Applicant's or agent's file reference  
**TS 1327 PCT**

**IMPORTANT NOTIFICATION**

International application No.  
**PCT/EP2004/050499** ✓

International filing date (day/month/year)  
**13.04.2004**

Priority date (day/month/year)  
**15.04.2003**

Applicant  
**SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.**

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary report on patentability and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.
4. **REMINDER**

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary report on patentability. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

The applicant's attention is drawn to Article 33(5), which provides that the criteria of novelty, inventive step and industrial applicability described in Article 33(2) to (4) merely serve the purposes of international preliminary examination and that "any Contracting State may apply additional or different criteria for the purposes of deciding whether, in that State, the claimed inventions is patentable or not" (see also Article 27(5)). Such additional criteria may relate, for example, to exemptions from patentability, requirements for enabling disclosure, clarity and support for the claims.

Name and mailing address of the international preliminary examining authority:



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## PATENT COOPERATION TREATY

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REC'D 22 JUN 2005


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**INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY**

(Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference TS 1327 PCT	<b>FOR FURTHER ACTION</b> See Form PCT/IPEA/416	
International application No. PCT/EP2004/050499	International filing date (day/month/year) 13.04.2004	Priority date (day/month/year) 15.04.2003
International Patent Classification (IPC) or national classification and IPC C01B3/38, B01J8/06, B01J8/00		
Applicant SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.		
<p>1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 6 sheets, including this cover sheet.</p> <p>3. This report is also accompanied by ANNEXES, comprising:</p> <p>a. <input checked="" type="checkbox"/> sent to the applicant and to the International Bureau a total of 3 sheets, as follows:</p> <p><input checked="" type="checkbox"/> sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions).</p> <p><input type="checkbox"/> sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box.</p> <p>b. <input type="checkbox"/> (sent to the International Bureau only) a total of (indicate type and number of electronic carrier(s)) , containing a sequence listing and/or tables related thereto, in computer readable form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions).</p>		
<p>4. This report contains indications relating to the following items:</p> <p><input checked="" type="checkbox"/> Box No. I Basis of the opinion</p> <p><input type="checkbox"/> Box No. II Priority</p> <p><input type="checkbox"/> Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability</p> <p><input type="checkbox"/> Box No. IV Lack of unity of invention</p> <p><input checked="" type="checkbox"/> Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement</p> <p><input type="checkbox"/> Box No. VI Certain documents cited</p> <p><input type="checkbox"/> Box No. VII Certain defects in the international application</p> <p><input type="checkbox"/> Box No. VIII Certain observations on the international application</p>		
Date of submission of the demand  21.01.2005	Date of completion of this report  20.06.2005	
Name and mailing address of the International preliminary examining authority:   European Patent Office - P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Tx: 31 651 epo nl Fax: +31 70 340 - 3016	Authorized Officer  Van der Poel, W  Telephone No. +31 70 340-3760	



**INTERNATIONAL PRELIMINARY REPORT  
ON PATENTABILITY**

International application No.  
PCT/EP2004/050499

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**Box No. I Basis of the report**

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1. With regard to the **language**, this report is based on the international application in the language in which it was filed, unless otherwise indicated under this item.
- ☐ This report is based on translations from the original language into the following language , which is the language of a translation furnished for the purposes of:
- ☐ international search (under Rules 12.3 and 23.1(b))
  - ☐ publication of the international application (under Rule 12.4)
  - ☐ international preliminary examination (under Rules 55.2 and/or 55.3)
2. With regard to the **elements\*** of the international application, this report is based on *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report):*

**Description, Pages**

1-29 as originally filed

**Claims, Numbers**

1-16 received on 14.02.2005 with letter of 14.02.2005

**Drawings, Sheets**

1/5-5/5 as originally filed

- ☐ a sequence listing and/or any related table(s) - see Supplemental Box Relating to Sequence Listing
3. ☐ The amendments have resulted in the cancellation of:
- ☐ the description, pages
  - ☐ the claims, Nos.
  - ☐ the drawings, sheets/figs
  - ☐ the sequence listing (*specify*):
  - ☐ any table(s) related to sequence listing (*specify*):
4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).
- ☐ the description, pages
  - ☐ the claims, Nos.
  - ☐ the drawings, sheets/figs
  - ☐ the sequence listing (*specify*):
  - ☐ any table(s) related to sequence listing (*specify*):

\* If item 4 applies, some or all of these sheets may be marked "superseded."

**INTERNATIONAL PRELIMINARY REPORT  
ON PATENTABILITY**

International application No.  
PCT/EP2004/050499

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**Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

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**1. Statement**

Novelty (N)	Yes: Claims	3-16
	No: Claims	1, 2
Inventive step (IS)	Yes: Claims	5-16
	No: Claims	1-4
Industrial applicability (IA)	Yes: Claims	1-16
	No: Claims	

**2. Citations and explanations (Rule 70.7):**

**see separate sheet**

**Re Item I**

**Basis of the report**

1. Claim 5 has been amended in line 13. The claim now specifies that there is a plurality of parallel positioned tubes. Basis for this amendment can be found on page 9, lines 16-18 in combination with figure 3.

**Re Item V**

**Reasoned statement with regard to novelty, inventive step or industrial applicability;  
citations and explanations supporting such statement**

Reference is made to the following documents:

D1: WO-A-01/34287 (Metallgesellschaft AG)  
D2: WO-A-88/01983 (L & C Steinmüller GmbH)  
D3: DE-A-3345088 (Linde AG)

**Apparatus claims 1-4:**

- 1.1. The present application does not meet the criteria of Article 33(1) PCT, because the subject-matter of claims 1 and 2 is not new in the sense of Article 33(2) PCT.

Document D1 discloses a reactor for dehydrating hydrocarbons in a tube reactor. Catalyst is filled in the tube. A smaller empty tube is present within the catalyst tube. Heating of the reactor takes place, both from the outside of the tube and from the inner tube. In the example a catalyst of Pt on alumina is used (see example; figure).

It would appear to the examining division that the catalyst is clearly suitable for reforming. The dehydration is performed at similar temperatures as catalytic steam reforming. The reactor of D1 is therefore suitable for performing a steam reforming reaction (see Guidelines C-III, 4.8).

The subject-matter of claims 1 and 2 is not novel.

Document D2 discloses a tubular steam reformer. Catalyst is packed in the shell, whereas the heating fluid flows through the tubes (see claim 1; figure 1).

The subject-matter of claim 1 is not novel.

- 1.2.** The subject-matter of claims 3 and 4 appears to be obvious to the person skilled in the art. The mixing of a hot gas which contains hydrogen with another reformed gas is well-known in reforming technology. Especially the structural measures to achieve this (claim 3 is directed to the apparatus) are obvious to the person skilled in the art. Also the choice of material for the reactor tubes seems obvious for the person skilled in the art.

**Process claims 5-16:**

- 2.1.** The subject-matter of claim 5 appears to be novel and involve an inventive step (Article 33(1)-(3) PCT).

Document D3, which is considered to be the closest prior art for claim 5, discloses a process for the production of synthesis gas by partial oxidation of a hydrocarbon. In a tubular convective steam reformer further hydrocarbon is endothermically reformed, the heat for this endothermic reaction is supplied by passing the hot partial oxidation product around the tubes filled with catalyst (see claim 1; figures).

The only difference between claim 5 and document D3 lies in the fact that in claim 1 heating fluid passes through a passageway positioned within and along the axis of the one or more reactor tubes, whereas in D3 the heating fluid flows around the tubes.

The problem solved by this difference is to have less fouling from the heating medium, because of the higher velocities in the tubes.

Having the heating medium through the tubes in a steam reformer is known, however, from document D2. As already mentioned above, document D2 discloses a tubular steam reformer. Catalyst is packed in the shell, whereas the heating fluid

flows through the tubes (see claim 1; figure 1).

When the person skilled in the art would combine D3 with D2 he would arrive at a process combining partial oxidation and endothermic reforming, in which the catalyst is packed in a shell and the heating medium flows through the tubes. He would not arrive at the subject-matter of claim 5 where there is a plurality of tubes filled with catalyst in which there are smaller tubes through which the heat exchange medium flows.

The subject-matter of claim 5 is novel and involves an inventive step.

- 2.2.** The subject-matter of claims 6-16 is also considered to involve an inventive step, because these claims concern preferred embodiments of claim 5.

EPO - DG 1

14. 02. 2005

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(41)

NEW CLAIMS

1. Reactor vessel for performing a steam reforming reaction comprising:

- a vessel inlet for natural gas and steam,
- a vessel inlet for a hot gaseous medium,
- 5 - a vessel outlet for a gaseous product comprising the steam reforming product, and
- a reactor space comprising of a bed of steam reforming catalyst, which reactor space inlet is fluidly connected to the inlet for natural gas and steam and at
- 10 its outlet end fluidly connected with the outlet for the gaseous product,

wherein inside the catalyst bed a passageway is provided fluidly connected to the vessel inlet for the hot gaseous medium for passage of hot gaseous mixture counter

15 currently to the flow of reactants in the catalyst bed.

2. Reactor according to claim 1, wherein the reactor space is defined by one or more reactor tubes filled with a bed of steam reforming catalyst and wherein said reactor tube comprises one or more passageway(s) running

20 parallel to the axis of said reactor tube.

3. Reactor according to claim 2, wherein the steam reforming product exiting from the reactor tube, the vessel hot gaseous medium from its vessel inlet are both in fluid communication with the inlet of the passageways

25 such that in use a mixture of hot gaseous medium and the steam reforming product passes said passageway.

4. Reactor according to any one of claims 1-3, wherein the passageway is a tube made from a metal alloy, wherein the metal alloy comprises from 0 and up to 7 wt% iron,



between 0 and 5 wt% aluminium, from 0 up to 5 wt% silicon, from 20 up to 50 wt% chromium and at least 35 wt% nickel, wherein the nickel content balances the total to 100%.

5 5. Process for the preparation of hydrogen and carbon monoxide containing gas from a carbonaceous feedstock by performing the following steps:

10 (a) partial oxidation of a carbonaceous feedstock thereby obtaining a first gaseous mixture of hydrogen and carbon monoxide and

(b) catalytic steam reforming a carbonaceous feedstock in a Convective Steam Reformer comprising a tubular reactor provided with a plurality of parallel positioned tubes containing a reforming catalyst, wherein the required  
15 heat for the steam reforming reaction is provided by convective heat exchange between the steam reformer reactor tubes and a passageway positioned within and along the axis of the tubular reactor tubes through which passageway the effluent of step (a) flows counter-current  
20 to the gasses in the steam reformer tubes.

6. Process according to claim 5, wherein the gas velocity in the passageway is between 10 and 60 m/s.

25 7. Process according to any one of claims 5-6, wherein between 0 and 60 wt% of the steam reformer product as obtained in step (b) and the effluent of step (a) flows through the passageway.

8. Process according to any one of claims 5-7, wherein the  $H_2/CO$  molar ratio of the combined synthesis gas product of step (a) and (b) is between 1.5 and 3,  
30 preferably between 1.9 and 2.3.

9. Process according to any one of claims 5-8, wherein the steam to carbon molar ratio of the feed to step (b) is between 0.5 and 0.9.

10. Process according to claim 9, wherein the reforming catalyst comprises (a) an oxidic support material and (b) a coating comprising between 0.1 and 7.0 wt% of at least one of the metals of the group consisting of Pt, Ni, Pd and Co, preferably platinum; said support material comprising: (i) at least 80 wt% of  $ZrO_2$  which has been calcined at a temperature up to about 670 °C before the application of said coating; (ii) 0.5-10 mol% of at least one oxide selected from the group consisting of Y, La, Al, Ca, Ce and Si, preferably  $La_2O_3$ .

11. Process according to any one of claims 5-10, wherein the temperature of the metal wall surfaces of the passageways in step (b) is maintained below 1100 °C.

12. Process according to any one of claims 5-11, wherein the steam reforming product of step (b) is fed to step (a).

13. Process according to claim 12, wherein the steam reforming product of step (b) is fed to the upper half of a partial oxidation reactor vessel, said vessel provided with a burner at its upper end, and wherein the temperature in the upper half of the vessel is between 800 to 1050 °C.

14. Process according to any one of claims 12-13, wherein the mixture of the steam reformer product of step (b) and the product of the partial oxidation reaction of step (a) is subjected to an autothermal reformer step (c).

15. Process according to any one of claims 5-14, wherein hydrogen is recovered from the effluent of step (b).

16. Process according to any one of claims 5-15, wherein step (b) is performed in the reactor vessel according to any one of claims 1-4 of the present invention.

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